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Synthesis of vanillin in water by TiO_2 photocatalysis

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ABSTRACT

The photoproduction of vanillin is studied in aqueous medium starting from trans-ferulic acid, isoeugenol, eugenol or vanillyl alcohol by using both commercial and home prepared TiO_2 samples as photocatalysts and batch Pyrex photoreactors. The photo-oxidation at room temperature of these compounds produces vanillin with a selectivity ranging from 1.4 to 21 mol% with respect to the converted substrate. An investigation on the intermediates was performed in the case of trans-ferulic acid; for this substrate the most important intermediates were homovanillic acid, vanillyl mandelic acid, trans-caffeic acid, formic acid, acetic acid, and oxalic acid. The carbon mass balance, including CO_2 derived from the mineralization, was made for all of the substrates at irradiation times corresponding to the highest selectivity to vanillin. High closure of the carbon balance was obtained with vanillyl alcohol (ca. 90%) and trans-ferulic acid (ca. 80%).

1. Introduction

The exceptionally widespread utilization of vanillin in the food, cosmetic, pharmaceutical, nutraceutical and fine chemical industries makes vanillin one of the most important aroma and justifies the very large number of researches on the improvement of the production processes [1–5]. Currently, more than 99% of vanillin is produced by chemical synthesis and it is sold at a much lower price than the natural vanilla extract, which requires very long, complex and expensive procedures of cultivation of the plant, induced production of the beans, curing of the pods and extraction of the aromas. Unfortunately, the processes of chemical synthesis are not environmentally safe and the "bouquet" of the obtained "artificial" vanillin is usually considered to be of lower quality due to the lack of many trace components which substantially contribute to the flavour of the "natural" product. Besides, it must be taken into account that nowadays, in accordance with the preference of the consumers, the additives used in food, beverages, cosmetics and medicines should be natural substances. As a matter of fact, the utilization of eco-friendly aromas gives an extra value to the final product without severely affecting its cost since only very small quantities of these compounds are required to enrich the flavour. So, in the last decades many researchers investigated the possibility of producing vanillin through a green biotechnological route [3–15] to obtain a product, which, according to the European and USA rules, can be labelled as natural. Despite the very large number of works and studies which adopted this approach, till now only one commercial biotech product [16] is present in the market. In fact, even if future improvements are expected, the proposed biotechnology methods show some limitations such as relatively high costs, long production times, difficult purification and necessity of selected strains of microorganisms.

On the other hand, Palmisano et al. [17–26] and Zhao et al. [27,28] demonstrated that some aromas, namely aromatic aldehydes (e.g. benzaldehyde and paranisaldehyde), can be obtained from the corresponding alcohols by a photocatalytic process carried out in water at room temperature and atmospheric pressure. Heterogeneous photocatalysis is an advanced oxidation technology which till now has been generally utilized for water and air detoxification [29–32] and only in recent times is emerging as a very promising method for fine chemical synthesis [33–35]. Through this method the production of aromatic aldehydes takes easily place in relatively short times, at mild conditions, in aqueous suspension of TiO_2 powders, without any addition of chemicals except the starting alcohols. Very recently a patent has been submitted aimed to a possible industrial application [36]. In parallel some researchers found that the photocatalytic treatment of aqueous streams polluted by lignin and ferulic acid causes also the formation of small amounts of vanillin as an intermediate compound in the degradation path [37–40]. Also Qamar and Muneer [41] studied a photocatalytic process concerning vanillin, which was utilized as a model pollutant to be photocatalytically degraded in an aqueous solution.

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On this basis, the present work describes the synthesis of vanillin from different substrates by using the photocatalytic method. The chosen starting compounds are trans-ferulic acid, isoeugenol, eugenol and vanillyl alcohol. The first two are the same precursors which are usually considered for the biotechnological production of natural vanillin, since they are relatively cheap and can be also of natural origin.

2. Experimental

The photoreactivity experiments were carried out by using two commercial TiO_2 powders, i.e. P25 Degussa, ca. 80% anatase and 20% rutile (BET specific surface area, SSA: 50 $m^2\,g^{-1}$), and Merck, 100% anatase (SSA: 10 $m^2\,g^{-1}$), and two home prepared TiO_2 samples (HPC3 and HP0.5). Amounts of 0.2 and 0.8 $g\,L^{-1}$ were used for P25 Degussa and Merck, respectively, while 0.6 $g\,L^{-1}$ was employed for HPC3 and HP0.5. Due to the different optical properties of these powders, these amounts represented the lowest limits of photocatalyst load to obtain a negligible transmission of light. So the experiments are more comparable as all the entering photons were virtually absorbed by the suspension.

The preparation of anatase HPC3 sample (SSA: 35 $m^2\,g^{-1}$) resorts to a new sol–gel route ex $TiCl_4$ [19]. The hydrolyzation of $TiCl_4$ in water ($TiCl_4$/water = 1/11 v/v) produced a white sol that upon stirring for 10 h became a clear solution. Then the suspension was dried and the sol was heated at 673 K for 3 h obtaining a badly crystallized rutile phase.

As far as HP0.5 sample is concerned (SSA: 235 $m^2\,g^{-1}$) [17], the precursor solution was obtained by slowly adding 5 mL of $TiCl_4$ drop by drop into 50 mL of water in a beaker. During the addition, that lasted 5 min, the solution was magnetically stirred. After that, the beaker was closed and the mixing was prolonged for 12 h at room temperature obtaining a clear solution. This solution was transferred into a flask equipped with a Graham condenser, where it was boiled for 0.5 h to produce a white suspension of a solid constituted mainly by amorphous TiO_2 and crystalline phases of anatase (75%) and rutile (25%).

The experiments were carried out in aqueous suspensions with an initial substrate concentration of 0.5 mM or 1.0 mM, at natural pH by using a cylindrical photoreactor (CPR, internal diameter: 32 mm and height: 188 mm) containing 150 mL of aqueous suspension. It was irradiated by three external Actinic BL TL MINI 15 W/10 Philips fluorescent lamps whose main emission peak is in the near-UV region at 365 nm. The reactor was cooled by water circulating through a Pyrex thimble, so that the temperature of the suspension was about 300 K. The radiation intensity impinging on the suspension was measured by a radiometer Delta Ohm DO9721 with an UVA probe; the radiation power absorbed per unit volume of the suspension was about 0.76 mW/mL. Oxygen or air were continuously bubbled during the experiments and the lamps were switched on at time $t = 0$, after 0.5 h from the starting of the aeration. The values of substrate concentration before the addition of catalyst and before the starting of irradiation were measured in order to determine the substrate adsorption on the catalyst surface under dark conditions.

During the photoreactivity runs samples were withdrawn at fixed times; they were immediately filtered through 0.25 or 0.45 μm membranes (HA, Millipore) before analyses. The quantitative determination and identification of the starting molecules and their oxidation products were performed by means of a Beckman Coulter HPLC (System Gold 126 Solvent Module and 168 Diode Array Detector), equipped with a Phenomenex Synergi 4 μm Hydro-RP 80A column at 298 K or with a 3 μm Dionex Acclaim PA2. When the former column was used, the eluent consisted of a mixture of methanol and 1 mM trifluoroacetic acid aqueous solution (55:45 volumetric ratio for ferulic acid and vanillyl alcohol, 60:40 volumetric ratio for isoeugenol and eugenol). The flow rate was 0.6 $mL\,min^{-1}$ when trans-ferulic acid, isoeugenol and eugenol were tested or 0.4 $mL\,min^{-1}$ in the case of vanillyl alcohol. The eluent for the second column consisted of a mixture of water, acetic acid and acetonitrile (85:10:5 volumetric ratio) and the flow rate was 0.5 $mL\,min^{-1}$. A UV detector measured the absorbance at 260 nm for the runs with trans-ferulic acid, isoeugenol and vanillyl alcohol, whereas a wavelength of 280 nm was used for eugenol. Retention times and UV spectra of the compounds were compared with those of standards. Standards of vanillin, trans-ferulic acid, isoeugenol, eugenol, vanillyl alcohol and of the identified intermediates were purchased from Sigma–Aldrich with a purity of >99%.

The calibration curve of cis-ferulic acid, which is not commercially available, was obtained as follows: a solution of trans-ferulic acid was irradiated under UV light in order to transform it partially into cis-ferulic acid [42]. Samples were withdrawn every minute for three minutes and analyzed by HPLC. The concentration of the photoproduced cis-ferulic acid was calculated as the difference between the initial and the residual concentrations of trans-ferulic acid.

HPLC-Electrospray ionization mass spectrometry experiments (ESI-MS) were carried out on an Agilent Technologies (mod. B 1946) instrument with a quadrupole ion trap detector. Typical settings for MS acquisitions: needle voltage 4.5 kV, N_2 temperature 623 K, gas flow 12.5 $L\,min^{-1}$. Mass range was scanned from m/z 100 to m/z 2600 uma. The HPLC column used was a Phenomenex Gemini C18-3 μm–110 Å and the eluent was a mixture of water and acetonitrile (70:30 volumetric ratio).

Total organic carbon (TOC) analyses were carried out by a 5000 A Shimadzu analyser.

Ion chromatography (IC) analyses were carried out by a Dionex DX 120 instrument equipped with an IonPac AS14A (4 × 250 mm) column for determining the concentration of oxalate, formate and acetate ions. For oxalate ions the eluent was an 8.0 mM Na_2CO_3/1.0 mM $NaHCO_3$ buffer solution, whereas for formate and acetate ions a 1.0 mM Na_2CO_3/1.0 mM $NaHCO_3$ buffer solution.

In order to affect the process performance, some runs were carried out with a different photoreactor at almost equal energy absorbed per unit volume of the suspension (0.77 mW/mL). This photoreacting system consisted of an annular photocatalytic reactor (APR) with total slurry recirculation. The APR (inner tube diameter: 2.1 cm; height: 28 cm and annulus gap: 0.525 cm) with total recirculation was irradiated by an 8 W linear black-light Philips TL/08 lamp axially placed. The lamp emission peak is in the near-UV region at 365 nm and the intensity of the UVA radiation entering the suspension through the inner wall of annulus was about 2.5 $mW\,cm^{-2}$. The total volume of the suspension was 600 mL; it was continuously recirculated by a peristaltic pump with a flow rate of 680 $mL\,min^{-1}$. The reacting suspension was thermostated at 323 K. Aqueous suspension with 0.43 $g\,L^{-1}$ of Merck TiO_2 was ultrasonicated for 15 min before introduction into the APR; the initial concentration of all substrates was always 0.5 mM.

In some experiments with the APR system the final suspension was treated in order to separate vanillin. The recovery of vanillin was obtained by pervaporation through a non-porous PEBAX® 2533 membrane prepared by solvent casting. The vapours of vanillin, water and traces of organic compounds were frozen downstream in a liquid nitrogen trap. It can be noticed that in a pervaporation test run carried out at a temperature of 338 K, at a permeate pressure of 3 mbar and feeding a concentration of vanillin of about 6.5 mM, the transmembrane flux of vanillin was about 3.31 $g\,h^{-1}\,m^{-2}$. As it was observed also by Boddeker et al. [43], the permeate vapours of vanillin deposit as crystals at ambient temperature with a high degree of purity (higher than 99.8%) provided that the partial pressure of vanillin in the permeate is greater than about 5×10^{-5} mbar. By taking into account the enrichment factor [44] for vanillin, the

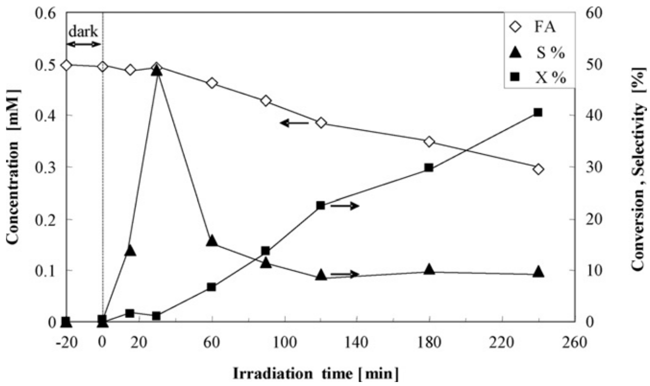


Fig. 1. Concentration and conversion (X) of ferulic acid (FA) versus irradiation time in the presence of air and selectivity (S) to vanillin for a representative run. Photocatalyst: Merck TiO_2 (0.8 g L^{-1}).

previous condition implies that crystals can deposit only if the concentration of vanillin in the liquid solution upstream the membrane exceeds 0.08 mM.

A digital camera Canon EOS 30D equipped with a Minolta Rokkor Bellows Micro 12.5 mm F2 lens was used to take microphotographs of the crystals of vanillin at a 14× magnification ratio.

3. Results and discussion

Fig. 1 reports the concentration of substrate, the conversion and the selectivity to vanillin (ratio between the produced vanillin and the reacted substrate) versus irradiation time for a representative run carried out with an initial trans-ferulic acid concentration of 0.5 mM in the presence of 0.8 g L^{-1} of Merck TiO_2 and of air. Notably, after starting the irradiation of the suspension, in a few minutes trans-ferulic acid partially transformed into cis-ferulic acid, as reported in the literature [45]. In this paper the generic term "ferulic acid" comprises both the isomers and the values of conversion and selectivity to vanillin are referred to the sum of the concentrations of the two isomers. From Fig. 1 it can be observed that the selectivity to vanillin slightly decreased (from 12 to ca. 11%) after ca. 8% conversion of ferulic acid and it remained virtually constant up to conversion of ca. 40%.

Table 1 reports the values of the highest selectivity to vanillin obtained from runs carried out by using a cylindrical photoreactor (CPR) with different substrates in the presence of both commercial and home prepared (HP) TiO_2 photocatalysts. These selectivity values were obtained in runs carried out by bubbling air or oxygen; the corresponding values of conversion and irradiation time are also reported. As expected for consecutive oxidation reactions, high values of selectivity to vanillin can be observed at the very beginnings of the runs; then the selectivity decreases but its figures do not change significantly in a wide range of substrate conversion. However, at higher conversions of the substrate the selectivity to vanillin decreases. Even if oxygen is a needed reactant, the selectivity values were almost unaffected by the oxygen concentration in the liquid phase. In fact the results obtained by bubbling pure oxygen were quite similar to the ones in presence of air.

For the experiments carried out in air the highest selectivity to vanillin (21% at a 15% conversion) was obtained when vanillyl alcohol was used. In the case of trans-ferulic acid and isoeugenol the selectivity to vanillin reached values of ca. 12% for conversions up to ca. 50%, while for eugenol a maximum of 5% was found for conversion up to 20%.

The presence of a double bond in the side chain of ferulic acid, isoeugenol and eugenol, but not in the vanillyl alcohol molecule, could be responsible of a stronger interaction between the reactant and the surface of HP photocatalyst, thus favouring the further (photo)oxidation steps of vanillin that gave rise to open ring intermediates and to CO_2 production, as confirmed by TOC analyses.

HP TiO_2 photocatalysts (HPC3 and HP0.5) were more selective than the commercial ones (P25 Degussa and Merck) when vanillyl alcohol was used, confirming results previously published by using aromatic alcohols [17–26]. An opposite behaviour was observed for the other three reactants: commercial TiO_2 photocatalysts showed to be more selective than the HP ones.

Due to the mild experimental conditions used for the preparation of HP photocatalysts, they are less crystalline and probably more defective than the commercial ones [17–26], therefore the presence of surface defects, i.e. Lewis acid sites, cannot be excluded. A clear clue supporting the occurrence of a strong surface acid–base reaction is the finding that HP photocatalysts became significantly yellow-ochre coloured when they were suspended in ferulic acid, isoeugenol or eugenol aqueous solutions. This chromatic effect was not so important with the commercial samples and it was always absolutely negligible when vanillyl alcohol was used.

The decrease of TOC concentration starts with the ignition of the lamp, indicating that also the CO_2 production begins at the same time. This behaviour indicates that CO_2 is obtained by two parallel pathways: in the first CO_2 is produced in the final step of consecutive oxidation reactions of species able to desorb from the catalyst surface and detected in the bulk of solution while in the second one the mineralization involves species which do not desorb from the surface. The occurrence of two parallel pathways indicates that the substrates interact with the TiO_2 surface in two different ways, i.e. that the TiO_2 surface possesses two types of sites which are specific for the occurrence of mineralization or partial oxidation [26].

Table 2 reports the values of the selectivity to vanillin and of the carbon mass balance for each substrate and for selected runs. For each substrate the calculation of the carbon balance was accomplished by transforming the concentrations of the identified intermediates into C atom concentration and by dividing these values by the initial C concentration of the substrate. These

Table 1
Irradiation time (t_{irr}), conversion (X) and selectivity to vanillin (S) for runs carried out by using different TiO_2 photocatalysts and CPR in the presence of pure oxygen or air.

		Trans-ferulic acid			Isoeugenol			Eugenol			Vanillyl alcohol		
		t_{irr} (min)	X (%)	S (%)	t_{irr} (min)	X (%)	S (%)	t_{irr} (min)	X (%)	S (%)	t_{irr} (min)	X (%)	S (%)
P25 Degussa	Oxygen	15	10	3	30	94	6.5	15	41	2.6	30	40	9
	Air	30	11	3	90	84	9.2	60	43	2.8	30	17	16
Merck	Oxygen	60	18	8	90	56	9.6	60	37	2.7	30	14	15
	Air	90	14	12	90	54	12	60	20	5	60	19	14
HPC3	Oxygen	60	98	1.5	–	–	–	–	–	–	60	16	13
	Air	90	42	2	15	27	8.3	30	23	3.5	90	15	21
HP0.5	Oxygen	60	97	1.6	–	–	–	–	–	–	60	11	20
	Air	120	96	1.4	15	71	1.5	15	30	1.2	120	13	16

Table 2
Carbon mass balance performed for some runs in the presence of air.

Substrate	Trans-ferulic acid	Isoeugenol	Eugenol	Vanillyl alcohol	Vanillyl alcohol
TiO_2 catalyst	Merck	Merck	Merck	Merck	HPC3
Irradiation time (min)	180	90	60	60	60
Conversion (%)	30.0	54.0	20.0	30.0	15.0
Selectivity to vanillin (%)	11.0	12.0	5.0	15.0	21.0
C as vanillin (%)	8.8	9.6	4.0	15.0	21.0
C as formic acid (%)	3.9	1.3	7.3	7.3	9.8
C as acetic acid (%)	1.3	2.4	28.6	5.8	7.5
C as oxalic acid (%)	0.7	0.0	0.0	0.0	0.0
C as trans-caffeic acid (%)	4.0	–	–	–	–
C as vanillyl mandelic acid (%)	27.5	–	–	–	–
C as homovanillic acid (%)	8.2	–	–	–	–
C as vanillic acid (%)	0.4	0.4	1.5	1.5	3.7
C as CO_2 (%)	25.0	4.2	8.3	18.7	47.9
Global C-balance (%)	79.8	20.3	50.7	48.3	89.9

Table 3
Adsorbed moles, conversion (X) and selectivity to vanillin (S) for ferulic acid and vanillyl alcohol.

Catalyst	Adsorption per unit SA (mmol m^{-2})	X (%) at t_{irr} = 15 min	S (%) at t_{irr} = 15 min
	Ferulic acid		
HP0.5	0.0020	58	0.46
HPC3	0.0018	43	1.08
P25	0.0015	6	1.61
Merck	0.0012	2	14
	Vanillyl alcohol		
P25	0.0040	11.5	18
HPC3	0.0010	5.2	20
Merck	0.0010	5.4	29
HP0.5	0.0003	2.0	41.5

calculations gave the C percentages reported in Table 2. In the global carbon balance the CO_2 concentration, calculated from TOC measurements, was also taken into account. In the case of trans-ferulic acid and vanillyl alcohol the closure of the balance is satisfactory, ca. 80% and ca. 90%, respectively, since most of the intermediates have been identified. The latter value is in accordance with previous work carried out by using similar aromatic alcohols [17–26].

Table 3 shows the values of adsorbed moles per unit surface area under dark conditions together with the conversion and selectivity values obtained after 15 min of irradiation for all of the used catalysts and for ferulic acid and vanillyl alcohol. Even if the adsorption in the dark is not representative of the adsorption conditions under irradiation [46], it can be noticed that the reactivity increases by increasing the adsorbed moles while the selectivity decreases.

The values of conversion and selectivity obtained by runs carried out by using the APR are reported in Table 4. In most cases the selectivities appear to be higher than the relevant values obtained with the CPR, suggesting that optimization of photoreactor configuration and of operative conditions may improve the process performance.

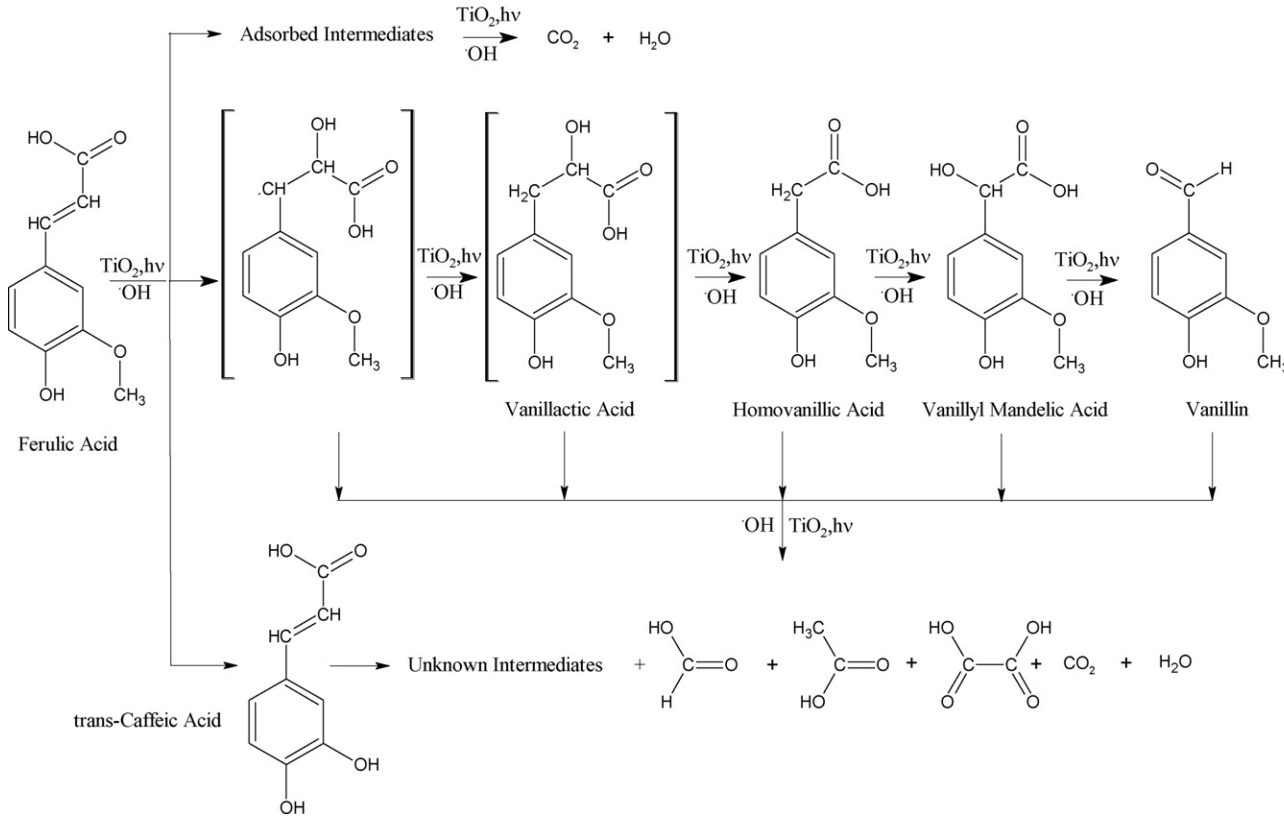
Schemes 1–4 report tentative mechanisms for the obtainment of vanillin starting from each of the four substrates. Unidentified or unstable species are reported in square brackets. A more thorough investigation on intermediate products obtained from trans-ferulic acid was carried out because this molecule offers some advantages as substrate; it is very soluble in water and, moreover, it can be easily obtained from different raw materials such as agricultural by-products. Scheme 1 shows the reaction pathways in the case of trans-ferulic acid. The presence of the intermediates reported in the scheme was validated by HPLC, mass spectrometry and ionic chromatography analyses. Homovanillic acid, vanillyl mandelic acid, formic acid, acetic acid, oxalic acid and CO_2 were found in the bulk of solution, while the presence of vanillactic acid was only hypothesized. Vanillic acid and trans-caffeic acid were also detected. The former derives from vanillin oxidation while the latter, obtained from trans-ferulic acid after substitution of $-OCH_3$ group by OH one, derives from a pathway that does not give rise to vanillin. It was observed that, after an initial increase, trans-caffeic acid quickly disappears. Vanillyl mandelic acid is known to be an intermediate from the production of vanillin from guaiacol. In that case vanillin is obtained by oxidative decarboxylation of vanillyl mandelic acid [45]. Among the various open ring species detected by HPLC, only formic, acetic and oxalic acids were identified so all the unidentified open ring compounds together with other aromatic unknown molecules are reported in the scheme as “unknown intermediates”.

For the irradiation times indicated in Table 1, oxalic acid was detected only with trans-ferulic acid; it was virtually absent when the other substrates were used. This finding could be related to the presence of the carboxylic group only in the side chain of trans-ferulic acid. Probably formation and stability of two carboxylic groups during the oxidation process is less likely for the three other reactants, at least under the experimental conditions used. Nevertheless traces of oxalic acid, possibly produced from the opening of the aromatic rings, were detected also for the other substrates for long lasting runs (ca. 5 h).

In order to check the reaction pathway hypothesized for trans-ferulic acid (see Scheme 1), some selected experiments were carried out starting from homovanillic acid (Fig. 2) or vanillyl mandelic acid (Fig. 3). In Fig. 2 it can be noticed the formation both of vanillyl mandelic acid and vanillin as the main products, while Fig. 3 shows that vanillyl mandelic acid produces vanillin. The amount of vanillin produced from vanillyl mandelic acid is higher than from homovanillic acid, indicating that vanillin is probably produced after the formation of vanillyl mandelic acid.

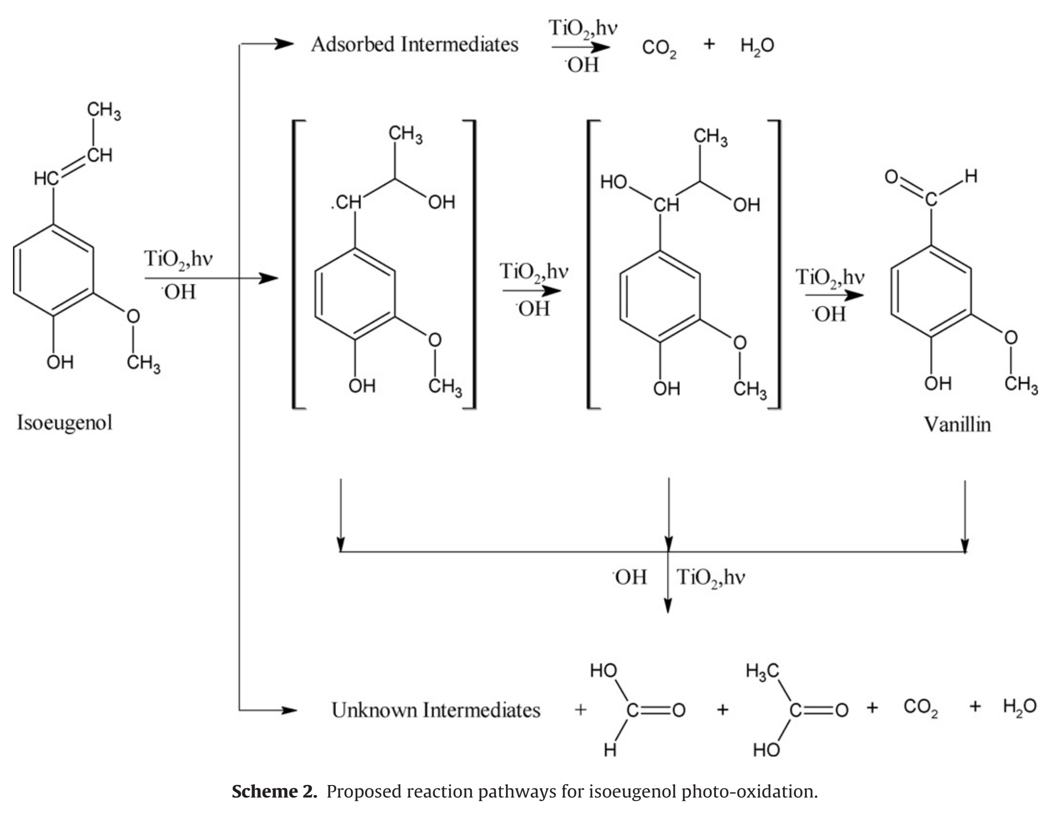
Table 4
Irradiation time (t_{irr}), conversion (X) and selectivity to vanillin (S) for runs carried out by using Merck TiO_2 and APR in the presence of air.

		Trans-ferulic acid			Isoeugenol			Eugenol			Vanillyl alcohol		
		t_{irr} (min)	X (%)	S (%)	t_{irr} (min)	X (%)	S (%)	t_{irr} (min)	X (%)	S (%)	t_{irr} (min)	X (%)	S (%)
Merck	Air	31	23	15.1	15	19	19.9	14	16	5.3	15	11	13

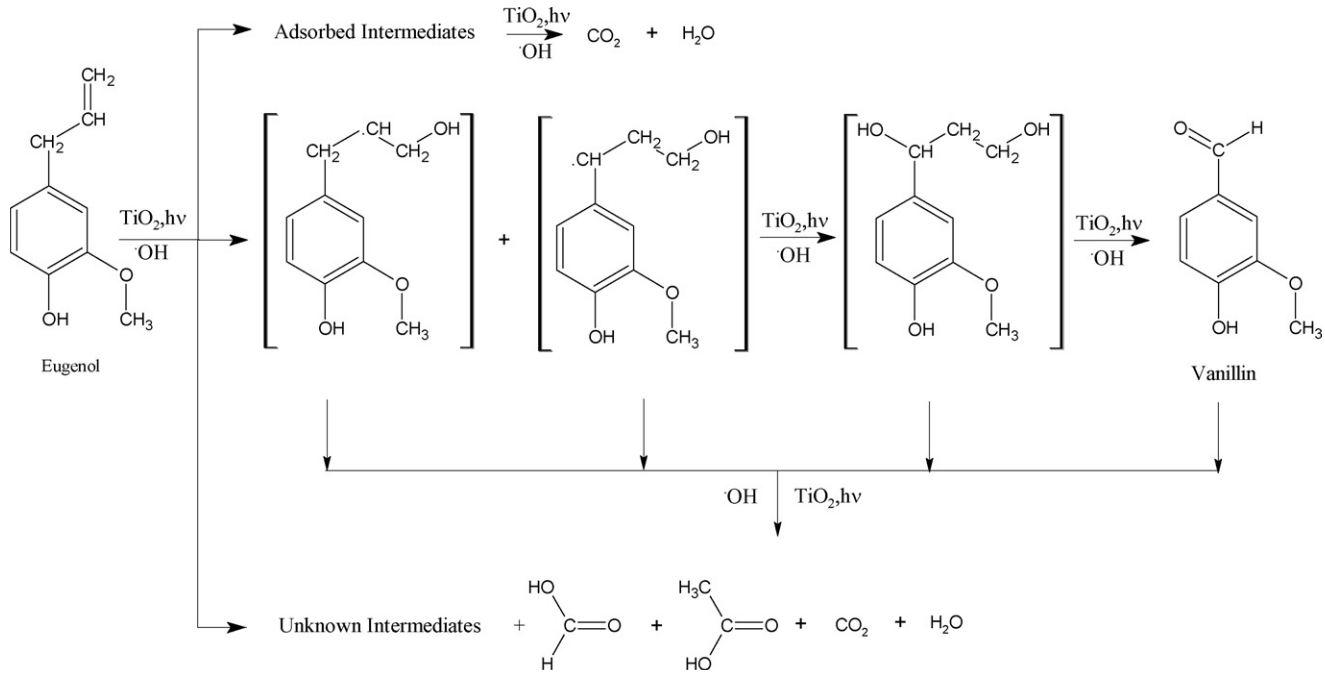


Scheme 1. Proposed reaction pathways for trans-ferulic acid photo-oxidation.

The vanillin produced by trans-ferulic acid oxidation was recovered from the aqueous suspension at the end of the runs by pervaporation through a non-porous membrane that completely retained the photocatalytic powders. The membrane showed to be very selective towards vanillin and almost impermeable with respect to most of the other organic compounds; only traces of trans-ferulic acid were actually detectable in the permeate. The permeate vapours of vanillin deposited as crystals at ambient



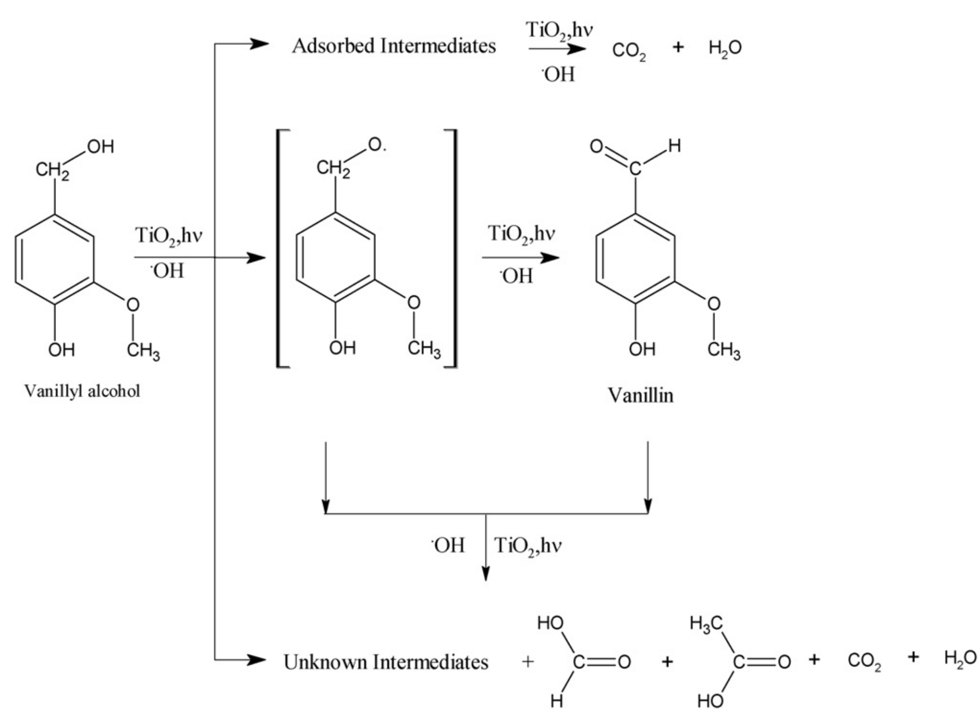
Scheme 2. Proposed reaction pathways for isoeugenol photo-oxidation.



Scheme 3. Proposed reaction pathways for eugenol photo-oxidation.

temperature with a high degree of purity (higher than 99.8%). In this simple way an almost complete purification from all the other compounds is obtained without the necessity to use complex extraction and re-crystallization procedures. In Fig. 4 vanillin crystals obtained from a representative run are shown.

The satisfactory results obtained by the recirculation photoreactor and the separation through a non-porous membrane suggest to investigate the combination of photocatalysis and pervaporation. In this coupled system the continuous subtraction of the photo-produced vanillin from the irradiated suspension should avoid its subsequent oxidation, this last being the main drawback of the batch photoreactors used in this work. In this way the process selectivity to vanillin should increase; work is in progress on this aspect.



Scheme 4. Proposed reaction pathways for vanillyl alcohol photo-oxidation.

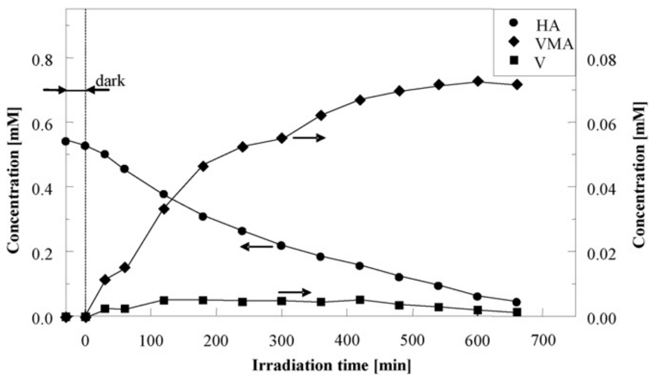


Fig. 2. Concentration of homovanillic acid (HA), vanillyl mandelic acid (VMA) and vanillin (V) versus irradiation time. Photocatalyst: Merck TiO_2 0.8 g L^{-1}.

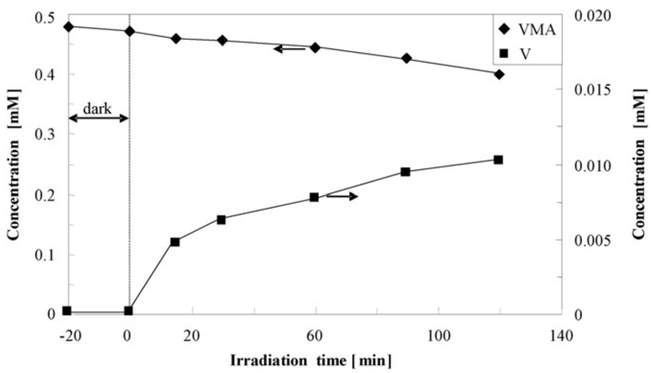


Fig. 3. Concentration of vanillyl mandelic acid (VMA) and vanillin (V) versus irradiation time. Photocatalyst: Merck TiO_2 0.8 g L^{-1}.

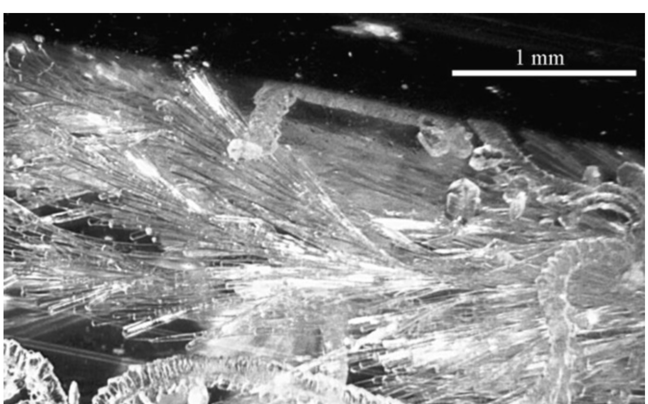


Fig. 4. Microphotography of vanillin crystals obtained by pervaporation.

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